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Directed growth of multiwalled carbon nanotubes from ordered porous silica structures†

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Ordered meso- and macroporous silica films can direct the growth of multiwalled carbon nanotubes from perpendicular to parallel to the substrate surface through control of the distribution of catalysts.

Carbon nanotubes (CNTs) with highly anisotropic physical and unique chemical properties are very attractive for applications in nanoscale devices.[1] To realize their potential as novel molecular components in nanodevices, controlled growth of carbon nanotubes is essential.[2] Recently, significant progress has been made in controlling the growth of multiwalled carbon nanotubes (MWNTs) on surfaces using the chemical vapor deposition (CVD) method.[3] Long and well-aligned MWNTs on large-scale substrates have been prepared.[4] Currently the most difficult problem in directed growth is the control of catalyst distribution and gas diffusion. This paper presents a simple method to control the distribution of catalysts and gas diffusion. By utilizing ordered ferriferous meso- or macroporous silica/aluminosilicate films with different structures, which are templated by block copolymer surfactants and polymer nanospheres,[5] MWNTs can be grown with their long axis either perpendicular or parallel to the substrate surface. Ordered meso- and macroporous silicas are excellent catalyst supports because they are mechanically and thermally stable and have high surface areas. Their large open pores allow efficient diffusion of the reactant and the hydrocarbon intermediates, and thus improve nanotube yield and purity because the rate-limiting step in CVD growth of carbon nanotubes is usually gas diffusion.[6] Meso- and macroporous silicas with ordered nanometer-sized two-dimensional (2D) or three-dimensional (3D) porous structures are ideal hosts for the host–guest chemistry system.[7] Generally, the catalysts are incorporated into the pores by impregnation or complex physical methods,[4c,8] and their drawback is that the external surface of the support is filled with catalysts despite the high internal surface area. Recently, Pinnavaia and coworkers found that ordered mesoporous silica could be templated by complexes of a nonionic polyethylene oxide surfactant with transition metal cations.[9] This points to a novel pathway to introduce transition metal catalysts into molecularly well-defined structures. This method is also more convenient than other commonly used methods such as electrochemical deposition into anodic aluminium oxide film[8b] and electron beam evaporation into porous silicon.[4c] Herein we report a novel approach to directly grow MWNTs by controlling the distribution of transition metal catalysts through use of different meso- and macroporous silica structures. It is noted that 3D ordered macroporous silica is utilized as a growth guide for MWNTs for the first time. Unlike the previous work on a macroporous silicon support[4c] where the catalyst was sputtered on the upper surface of the support, catalytic ferric oxides here were mixed into the silica macropore walls. It is easy for the reactants to reach the surface of the catalyst through a 3D macroporous structure and this leads to high catalyst efficiency.

Ferriferous 3D cubic mesoporous silica SBA-16 films were prepared on a silicon wafer by dip coating using poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymer Pluronic F127 ($M_{\mathrm{av}} = 12600$) $\mathrm{EO_{106}PO_{70}EO_{106}}$ as a structure-directing agent with a solution of typical molar composition: 1 TEOS/$(6–11) \times 10^{-3}$ $\mathrm{EO_{106}PO_{70}EO_{106}}$/1–2 H_2O/0.005–0.015 HCl/3–4 EtOH/corresponding moles of $\mathrm{FeCl_3 \cdot 6H_2O}$.[10] TEOS and EtOH stand for tetraethylorthosilicate and ethanol respectively. Ferriferous 2D hexagonal mesoporous silica SBA-15 films were similarly grown on the silicon wafer using a composition of 1 TEOS/$(4.8–34) \times 10^{-3}$ $\mathrm{EO_{20}PO_{70}EO_{20}}$ (Pluronic P123, $M_{\mathrm{av}} = 5800$)/4.4–12.2 H_2O/0.002–0.04 HCl/11–65 EtOH/corresponding moles of $\mathrm{FeCl_3 \cdot 6H_2O}$.[10] Ferriferous 2D hexagonal mesoporous aluminosilicate film (referred to as HMAS) was grown as follows. First 2.0 g (3.4×10^{-4} mol) of P123 and 0.21 g (7.7×10^{-4} mol) of $\mathrm{FeCl_3 \cdot 6H_2O}$ were dissolved in a 40 g 1 : 1 mixture of $\mathrm{CHCl_3}$ (0.105 mol) and tetrahydrofuran (THF) (0.25 mol) under moderate stirring. Then a prehydrolyzed solution of 3.0 g (1.3×10^{-2} mol) (3-glycidyloxypropyl)trimethoxysilane (GLYMO) and 0.6 g (2.9×10^{-3} mol) aluminium *sec*-butoxide in a 20 g 1 : 1 mixture of $\mathrm{CHCl_3}$ (0.052 mol) and THF (0.125 mol) was added.[11] The resultant mixture was used for the preparation of HMAS films. For the preparation of ferriferous macroporous silica,[12] a drop of a latex spheres (270 nm in diameter) solution was allowed to vaporize in the air on a silicon wafer. Then the sol solution containing: 3.51 g (1.69×10^{-2} mol) TEOS, 10 g (0.217 mol) EtOH, 0.84 g (2 mol l^{-1}) HCl, 1.103 g (6.13×10^{-2} mol) H_2O, 1.82 g (6.75×10^{-3} mol) $\mathrm{FeCl_3 \cdot 6H_2O}$ was added into the interstitial space of the latex spheres. The solvent was removed in a vacuum desiccator. All films were calcined at 550 °C in air for 6 h to remove block copolymer or latex beads template, followed by a reduction at 700 °C in a flowing stream of 10% H_2/N_2 (volume ratio) for 6 h. CVD growth for MWNTs was performed in a quartz tube at 700 °C with 2.5% acetylene/nitrogen (mole ratio). The growth time was typically 10–30 minutes.

CNTs can be easily grown on Fe-containing ordered mesoporous silica/aluminosilicate films (Fig. 1). The orientation of the CNTs depends on the structure of the ordered mesoporous films. Scanning electron microscopy (SEM) reveals the relationship between the orientation of the CNTs and the mesoporous structure and concentration of the catalyst. On 3D cubic mesoporous SBA-16 films, when Fe/silica $\geqslant 5.0$ wt%, the well-arrayed CNTs are perpendicular to

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†Electronic supplementary information (ESI) available: detailed experimental procedure. See http://www.rsc.org/suppdata/jm/b1/b104252c/

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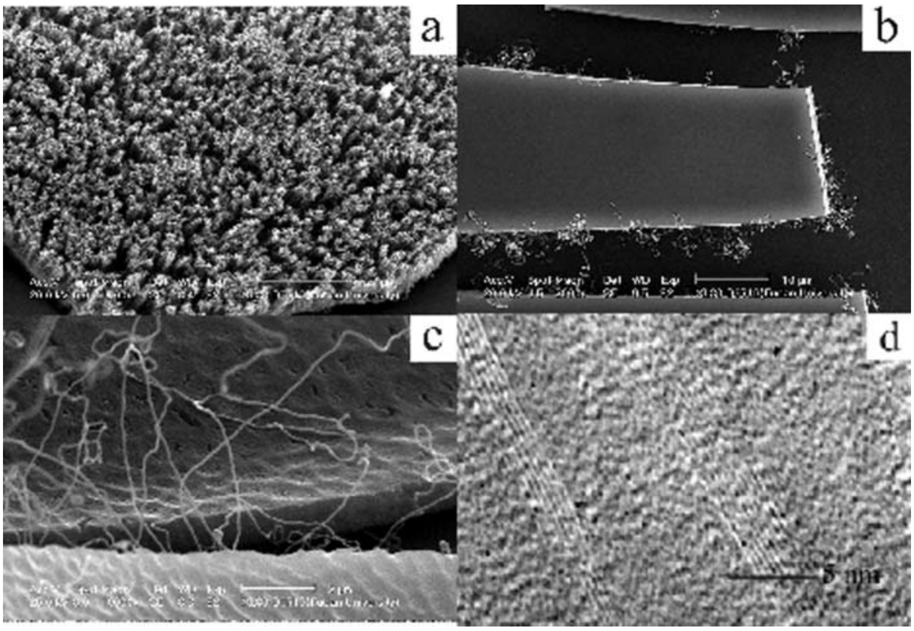

Fig. 1 SEM images (a,b,c) of oriented carbon nanotubes: (a) perpendicular to the substrate surface on a 3D ordered cubic mesoporous silica SBA-16 film ($Fe/SiO_2 = 5.0$ wt%); (b) and (c), parallel to the substrate surface on a 2D hexagonal mesoporous aluminosilicate HMAS film ($Fe/SiO_2 = 5.0$ wt%) with growth times of 10 and 30 min respectively. Carbon nanotubes were grown from the side of the cracked mesoporous films. (d) TEM image of typical obtained multiwalled nanotubes.

the substrate surface (Fig. 1a). When Fe/silica < 5.0 wt%, the CNTs are randomly oriented. It is expected that 3D cubic mesoporous silica SBA-16 films have significant numbers of nanopores (about 5–6 nm in diameter) perpendicular to the substrate surface,[13] providing an ordered array of catalyst sites. Because of its 3D nature, it also allows easy supply of gaseous reactants. When the concentration of the iron catalyst is high, the high number density of nucleation sites forces the growth in the direction perpendicular to the surface as this is the only direction in which space is readily available.[4a] In contrast, when the concentration of iron is low, space is available in all directions and the interaction between the CNTs is weak leading to randomly oriented CNTs.

When 2D ordered hexagonal mesoporous aluminosilicate HMAS films[14] with Fe/aluminosilicate $\leqslant 8$ wt% are used, CNTs with diameters of 20 nm can be easily grown parallel to the substrate surface (Fig. 1b, c). When Fe/aluminosilicate $\geqslant 15.0$ wt%, these tubes easily grow perpendicular to the substrate surface, like those growing on SBA-16 film. Similar to HMAS catalysts, 2D-hexagonal ordered mesoporous SBA-15 films with catalysts can also yield CNTs approximately parallel to the substrate plane. When the content of iron is low, mesoporous silica SBA-15 films have a 2D hexagonal mesostructure similar to that of HMAS[15] with aligned 1D channels parallel to the substrate plane. These results clearly show that the orientation of the CNTs depends on the channel structure of the mesoporous silica/aluminosilicate supports. The growth of CNTs on the 2D hexagonal mesoporous silica film also depends on the concentration of iron catalysts. These catalyst supports when combined with soft-lithography technology are potentially useful for the integration of carbon nanotubes into nanoscale electronic devices.

Transmission electron microscopy (TEM) images (Fig. 1d) show that the typically obtained CNTs are multiwalled nanotubes about 20 nm in diameter and 10 μm in length.

Previously, aligned nanotubes were obtained as a result of confined CVD nanotubes grown on the surface of disordered mesoporous silica or disordered commercial macroporous alumina membranes.[4,8b] In our process, growth of CNTs is confined to ordered mesoporous silica with different structures. Transition metal cations are known to form complexes with polymeric EO/PO units,[16] which template the self-assembly process and lead to ordered mesoporous silica.[9] After the ordered mesoporous silica films are calcined by slowly increasing temperature, Fe_2O_3 nanoparticles are formed and located in the pores. When the concentration of Fe(III) ions is high enough ($\geqslant 15$wt%), the Fe_2O_3 catalysts are located in the pore channels and in the walls.[17] When the Fe(III) concentration is high, X-ray diffraction measurements show that the pore structure becomes disordered, resulting in a disordered distribution of catalysts. Therefore, randomly oriented bundles of CNTs are formed. Large bundles of CNTs with sufficient rigidity result from van der Waals forces between neighboring nanotubes.[4]

When the ferriferous 3D macroporous silica is used as catalyst, the concentration of Fe(III) can be 40 wt% or higher while the ordered macroporous structure is still maintained and Fe(III) ions are dispersed in the silica wall. Due to its large inner surface area and inter-linked porous structure (Fig. 2a), well-aligned MWNTs can be easily obtained (Fig. 2b). As the concentration of Fe(III) increases, the diameter of obtained MWNTs increases from 10 nm to 50 nm, and the growing time to the same diameter size for the MWNTs can be reduced. This catalyst shows obvious high efficiency. These results suggest that the rate-limiting step in CNT growth is the gas diffusion, and 3D macroporous silica can provide sufficient space to allow easy gas diffusion, leading to highly efficient CNT growth.

In summary, the results shown above demonstrate that directed growth of well-aligned CNTs can be achieved by utilizing ordered meso- and macroporous silica/aluminosilicate as catalyst supports. This provides a simple pathway to incorporate the catalyst into the pores and to control the gas diffusion and the distribution of catalysts through metal coordination compounds with polymeric PO/EO units of surfactants, and furthermore to control the directed growth of CNTs. We have successfully used this pathway to prepare patterned well-aligned carbon nanotubes by combining it with soft-lithography technology.[18] Therefore, we believe that the ordered meso- and macroporous materials synthesized by using amphiphilic triblock copolymers containing PO/EO surfactants and polymer nanospheres provide a novel pathway to

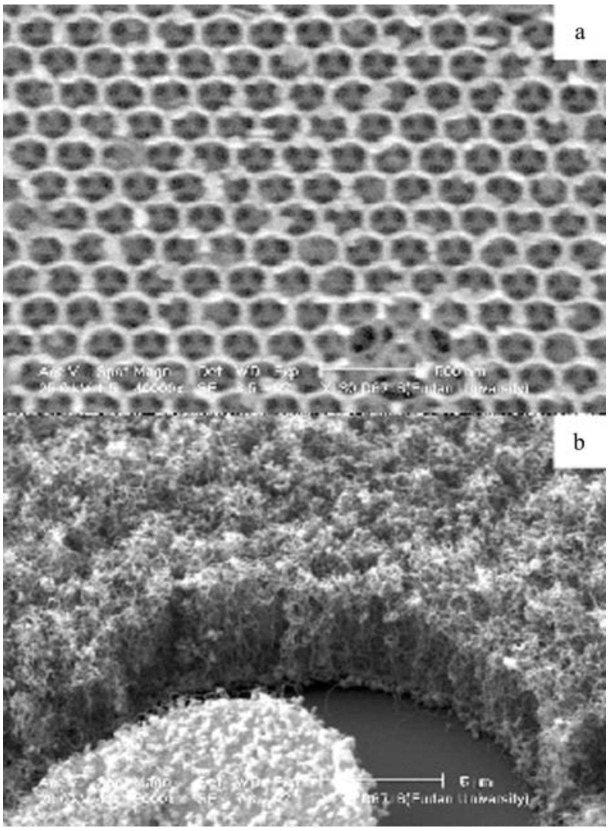

Fig. 2 (a) SEM image of ferriferous 3D macroporous silica. Latex spheres have been removed and face-centered cubic ordered pores are shown. (b) SEM image of aligned carbon nanotubes grown on the macroporous film.

controlled growth of CNTs. This exhibits exciting possibilities for future applications in the fabrication of electronic devices of CNTs.

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13 The highly ordered 3D cubic mesostructure of SBA-16 films is confirmed by X-ray diffraction (XRD), TEM and N_2 adsorption/desorption measurements. The XRD for the cubic mesoporous SBA-16 films shows a well-resolved diffraction pattern with at least seven reflection peaks which can be indexed to the *Im*3*m* space group ($a = 18.2$ nm). TEM images and 2D XRD show that the SBA-16 films have a well-ordered cubic mesostructure and a preferred orientation where the (100) plane is parallel to the substrate surface. Calcined cubic SBA-16 films exhibit a large pore size of 12.0 nm, a high BET surface area of 1100 $m^2\ g^{-1}$, and a pore volume of 1.03 $cm^3\ g^{-1}$.

14 XRD patterns of mesoporous aluminosilicate HMAS films show three diffraction peaks at low angle ($2\theta = 0.7$–$5.0°$) which can be indexed as the (100), (200) and (300) reflections, suggesting that HMAS films have a highly ordered 2D hexagonal (*p6m*) mesostructure ($a = 11.9$ nm) with its pore channels oriented parallel to the substrate surface. N_2 adsorption/desorption measurements show that the calcined films have a large pore size of 8.4 nm, a BET surface area of 256 $m^2\ g^{-1}$, and a pore volume of 0.53 $cm^2\ g^{-1}$.

15 TEM images and XRD patterns show that mesoporous SBA-15 films have a well-ordered 2D hexagonal mesostructure with preferred orientation. The XRD patterns show five diffraction peaks at low angles ($2\theta = 0.7$–$5.0°$) which can be indexed as the (100), (200), (300), (400) and (500) reflections ($a = 11.9$ nm). TEM measurements further confirm that the films have a well-ordered 2D hexagonal structure (*p6m*) with its pore channels aligned parallel to the substrate surface. N_2 adsorption/desorption measurements show that the calcined SBA-15 films have a large pore size of 8.2 nm, a high BET surface area of 810 $m^2\ g^{-1}$, and a large pore volume of 1.26 $cm^3\ g^{-1}$.

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